

# $1/T_1$ nuclear relaxation time of $\kappa - (BEDT - TTF)_2Cu[N(CN)_2]Cl$ : effects of magnetic frustration

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We study the role played by the magnetic frustration in the antiferromagnetic phase of the organic salt  $\kappa - (BEDT - TTF)_2Cu[N(CN)_2]Cl$ . Using the spatially anisotropic triangular Heisenberg model we analyze previous and new performed NMR experiments. We compute the  $1/T_1$  relaxation time by means of the modified spin wave theory. The strong suppression of the nuclear relaxation time observed experimentally under varying pressure and magnetic field is qualitatively well reproduced by the model. Our results suggest the existence of a close relation between the effects of pressure and magnetic frustration.

## I. INTRODUCTION

The interplay between frustration and strong correlation in electronic systems has become a central issue in condensed matter theory. Among the compounds which manifest this interplay are the quasi-bidimensional organic salts  $(BEDT - TTF)_2X$  [1] and the cobaltate compounds  $Na_xCoO_2$  [2]. In particular, the  $\kappa$  family of the organic salts displays a molecular arrangement characterized by a strong dimerization of BEDT-TTF molecules in anisotropic triangular layers. The presence of the monovalent anion  $X$  introduces a hole into each dimer rendering the antibonding molecular orbital of the dimer half filled. Recently, the phase diagram for  $X = Cu[N(CN)_2]Cl$  (hereafter,  $\kappa - Cl$ ) has been obtained [3] with paramagnetic insulating (PI), antiferromagnetic insulating (AF), superconducting (SC), and metallic (M) phases (Fig. 1). The boundary separating the PI from the metallic phase is a first order Mott transition with a critical endpoint at around  $40^\circ K$  and 280 bar [4]. On the other hand, within a range of pressure of 200 – 400 bar, there is a coexistence region of AF and SC phases which is not shown in Fig. 1. Regarding the insulating phases, as temperature is decreased, there is a transition from PI to an antiferromagnetic phase with a commensurate magnetic order, while the effect of pressure is to decrease the Néel temperature. It is worth noting that

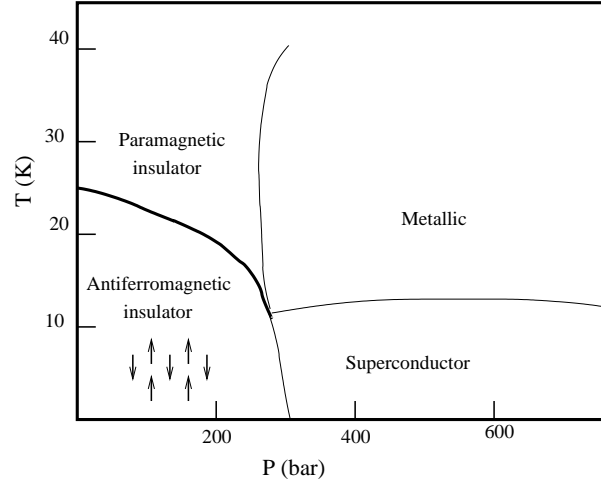


FIG. 1: Schematic temperature vs pressure phase diagram of  $\kappa - Cl$  obtained in ref. [3]. The thick line represents the magnetic transition of interest for the present study.

the paramagnetic insulating phase is always in between the antiferromagnetic and the metallic phases. This absence of boundary confirms the lack of itinerant AF in this organic salt. For this reason, a description of the PI-AF transition in terms of interacting localized spins on dimers lying on a triangular lattice deserves further investigation. It can be hypothesized that the decrease of the Néel temperature with pressure may originate from the pressure-induced increase of the magnetic frustration. While the interplay between pressure, electronic correlation, and frustration has

not yet been elucidated, due to the complex structure of the  $\kappa$  compounds, some results in the literature suggest that strong correlation and pressure-induced frustration is at play in the  $\kappa$  compounds. For example, it is generally believed that the application of hydrostatic or chemical pressure (i.e., change of anion  $X$  composition) reduces the ratio  $U/W$ , where  $U$  is the effective dimer Coulomb repulsion and  $W$  is the bandwidth (the pressure enhances the inter-dimer integral transfer  $t$ [5]), therefore driving the system through a Mott transition[1]. Very recently, several authors, within the context of Hubbard models, have proposed a RVB theory of superconductivity for the  $\kappa$  organic compounds, and they have emphasized the role of frustration in the transition from the AF to the metallic phase through a superconducting state. In particular, Powell and McKenzie[6] pointed out that the Mott transition can be driven by an increase of frustration even at fixed  $U/W$ , whereas, Gan *et al.*[7] proposed that the effect of pressure in the phase diagram is to decrease  $U/W$  and/or to increase the frustration.

Regarding the insulating phase, the proper effective Hamiltonian proposed to describe the antiferromagnetic phase of the  $\kappa$  family is the spatially anisotropic Heisenberg model on a triangular lattice where each site represents a dimer[1], and the exchange interaction is  $J = 4t^2/U$ . The zero temperature phase diagram of this model has been studied with spin wave theory [8], Schwinger bosons [9], and series expansion [10], and it shows collinear AF, disordered, incommensurate and commensurate spiral phases depending on magnetic frustration. The AF magnetic phase of the  $\kappa - Cl$  compound seems to be located at the collinear AF side of the diagram. Even though the ground state properties of this frustrated microscopic model have been investigated in the last years, its relevance to describe the insulating phase of the  $\kappa$  family has been little explored in the literature[11].

Here we compare qualitatively the predictions of the aforementioned frustrated model with our measurements of the magnetic field dependence of the  $1/T_1$  relaxation time for the  $\kappa - Cl$  compound. We also compare our theoretical results with previous measurements of  $1/T_1$  performed under varying pressure[3]. We have solved the model using the modified linear spin wave theory in order to avoid both, the presence of long range order –due to low dimensionality– and the divergence of the number of magnons at finite temperature. This can be achieved by imposing a zero magnetization constraint through a Lagrange multiplier [12]. The modified spin wave theory recovers the expected behavior of several thermodynamic properties for an ample range of temperature and frustration. The  $1/T_1$  nuclear relaxation time has been computed taking into account the Raman processes which, by energy conservation considerations, involve two magnons (simultaneous creation and destruction of magnons)[13].

Experimentally, the location of the  $1/T_1$  peak signals the magnetic ordering temperature. The responsible of such magnetic order in this highly anisotropic compound are the strong correlations or the 2D spin fluctuations present in the organic layers, while the existence of a finite ordering temperature is due to 3D residual interactions. On the other hand, our calculation of the relaxation time is performed in a two dimensional model, and this fact prevents the existence of an actual phase transition. However, since our model takes into account the relevant 2D magnetic interactions, the crossover that gives rise to the  $1/T_1$  peak corresponds to what actually happens in the critical region of the real 3D compound.

Our main finding is that the frustrated spin model reproduces qualitatively well the effects of pressure and magnetic field on the  $1/T_1$  relaxation time of the  $\kappa - Cl$  compound. These results suggest the idea that frustration and pressure are closely related. Furthermore, the experimental and theoretical results show a strong suppression of the nuclear relaxation time with increasing magnetic field. This behavior, characteristic of slow spin dynamics, signals the presence of magnetic frustration in the  $\kappa$  compound.

The article is organized as follows: In Sec. II we develop the modified spin wave theory for the microscopic model and we study the reliability of the approximation by computing several thermodynamic observables. In Sec. III we analyze the effects of pressure and magnetic field on the  $1/T_1$  relaxation time of the AF phase of the  $\kappa - Cl$  compound, using the frustrated spin model. The concluding remarks are presented in Sec. IV.

## II. MODIFIED SPIN WAVE THEORY

The spatially anisotropic Heisenberg model on the triangular lattice is:

$$H = \sum_{\mathbf{r}, \delta} J_{\delta} \mathbf{S}_{\mathbf{r}} \cdot \mathbf{S}_{\mathbf{r}+\delta} \quad (1)$$

where each site represents a half filled dimer, and  $J_{\delta}$  are the exchange antiferromagnetic interactions,  $J_{\delta_1} = J_{\delta_2} = J$  and  $J_{\delta_3} = J'$  (see Fig. 2).

Within the linear spin wave theory the ground state of this model presents two kind of phases[8], the collinear, characterized by the  $\mathbf{Q}_{\text{col}} = (0, 2\pi/\sqrt{3})$  wave vector (as shown in Fig. 2), stable in the region  $0 \leq J'/J \leq 0.5$ , and the incommensurate spiral, characterized by  $\mathbf{Q}_{\text{sp}} = (2Q, 0)$ , where  $Q = \cos^{-1}(J/2J')$ , and stable in the region  $0.5 \leq J'/J \leq \infty$ . In previous NMR experiments of  $\kappa - Cl$  it was observed a splitting of the spectra into a discrete

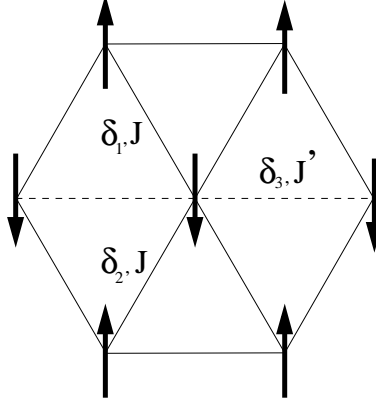


FIG. 2: Néel order characterized by the magnetic wave vector  $\mathbf{Q}_{\text{col}} = (0, 2\pi/\sqrt{3})$ . The dotted lines represent the frustrated bonds.

number of lines which can be identified with a commensurate AF order lying in the organic layers[14]. So, in what follows we concentrate our attention on the values of frustration interaction that give rise to a collinear structure  $\mathbf{Q}_{\text{col}} = (0, 2\pi/\sqrt{3})$ . Since we are interested in computing thermodynamic quantities, the 2D spin wave theory must be extended to finite temperatures. This is not straightforward for two reasons: i) the number of excited magnons diverges within the linear spin wave theory and, ii) the magnetization of a 2D Heisenberg model must be zero, in agreement with Mermin-Wagner's theorem[15]. In order to reconcile these two points, following Takahashi[12], it is imposed a condition on the number of magnons - $S$  magnons per site- that gives rise to a zero magnetization. Although the conventional spin wave theory relies on the existence of long range order, the elementary excitations at finite temperatures of a low dimensional antiferromagnet still resemble the spin waves excitations of the ordered ground state. The zero magnetization condition[12] turns out

$$S - \frac{1}{N} \sum_{\mathbf{k}} \mathbf{a}_{\mathbf{k}}^{\dagger} \mathbf{a}_{\mathbf{k}} = 0,$$

where the  $a$ 's are the bosonic operators of the Holstein-Primakov spin representation, and  $N$  is the number of lattice sites. Here there is one kind of boson because we have assumed that all spins are pointing in the  $z$ - direction of a local spin quantization axis as in ref[8]. Once this condition is included by means of a Lagrange multiplier  $\lambda$  in the spin wave version of Hamiltonian(1), it can be diagonalized by means of a Bogolyubov transformation  $\alpha_{\mathbf{k}} = u_{\mathbf{k}} \mathbf{a}_{\mathbf{k}} - v_{\mathbf{k}} \mathbf{a}_{-\mathbf{k}}^{\dagger}$ . After some algebra,

$$H = \sum_{\mathbf{k}} \omega_{\mathbf{k}} (n_{\mathbf{k}} + \frac{1}{2}) - \lambda N (S + \frac{1}{2}) + E_c (1 + \frac{1}{S})$$

with a magnon energy dispersion

$$\omega_{\mathbf{k}} = (S/2) \sqrt{\gamma_{\mathbf{k}}^2 - \beta_{\mathbf{k}}^2},$$

and

$$\begin{aligned} \gamma_{\mathbf{k}} &= 2 \sum_{\delta} J_{\delta} \left\{ \cos \mathbf{k} \cdot \delta \cos^2 \frac{\mathbf{Q} \cdot \delta}{2} - \cos \mathbf{Q} \cdot \delta \right\} + \lambda/S \\ \beta_{\mathbf{k}} &= -2 \sum_{\delta} J_{\delta} \sin^2 \frac{\mathbf{Q} \cdot \delta}{2} \cos \mathbf{k} \cdot \delta. \end{aligned}$$

$E_c = N S^2 \sum_{\delta} J_{\delta} \cos \mathbf{Q} \cdot \delta$  is the classical energy and  $n_{\mathbf{k}}$  is the Bose occupation number. The Lagrange multiplier  $\lambda$  acts as a chemical potential, opening a gap in the magnon dispersion. By minimizing the free energy of the system a self consistent equation for  $\lambda$  can be obtained:

$$\frac{1}{2} \sum_{\mathbf{k}} (1 + 2n_{\mathbf{k}}) (\gamma(\mathbf{k})/\omega_{\mathbf{k}}) = 1. \quad (2)$$

In the modified spin wave theory the resolution of Eq. (2) leads to a temperature dependent  $\lambda$ , and then to a temperature dependent excitation spectrum which takes into account the effect of entropy on the system[12]. In order to test the reliability of the modified spin wave theory, we have computed different finite temperature magnitudes like structure factor, uniform susceptibility, and specific heat. The static structure factor can be calculated as the Fourier transform of the mean value of the spin-spin correlation  $S(\mathbf{q}) = \sum_{\mathbf{r}} e^{i\mathbf{q}\cdot\mathbf{r}} \langle \mathbf{S}_0 \cdot \mathbf{S}_{\mathbf{r}} \rangle$ . Although the modified spin wave theory is not rotationally invariant, it can be shown that the contribution of the longitudinal spin fluctuations  $-S^{zz}(\mathbf{q})$  reproduces exactly the structure factor of a rotationally invariant theory[16]. The Holstein-Primakov transformation for the spin operators is replaced and a mean field decoupling is performed to terms of four boson operators. By considering only those contractions that conserve total spin[12], we finally obtain,

$$S(\mathbf{q}) = -\frac{1}{4} + \frac{1}{N} \sum_{\mathbf{k}} [(u_{\mathbf{k}+\mathbf{q}}^2 + v_{\mathbf{k}+\mathbf{q}}^2)(u_{\mathbf{k}}^2 + v_{\mathbf{k}}^2) - 4u_{\mathbf{k}} v_{\mathbf{k}} u_{\mathbf{k}+\mathbf{q}} v_{\mathbf{k}+\mathbf{q}}] \times (n_{\mathbf{k}+\mathbf{q}} + \frac{1}{2})(n_{\mathbf{k}} + \frac{1}{2}),$$

while the static uniform susceptibility is given by

$$\chi = \frac{1}{T} \sum_r \langle S_0^z S_r^z \rangle = \frac{1}{3T} S(\mathbf{q} = \mathbf{0}). \quad (3)$$

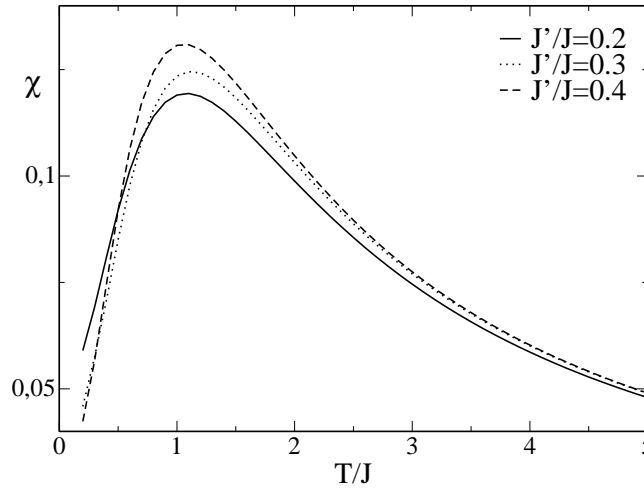


FIG. 3: Static uniform susceptibility versus temperature for several values of frustration.

In Fig. 3 we show the uniform susceptibility as a function of temperature for several values of frustration. It has a rounded peak located at  $T \sim J$  that signals the onset of the AF Néel correlations. In an actual (3D) case this would imply AF long range order. The effect of frustration is to slightly decrease the temperatures at which the peaks occur[11]. At larger temperatures a Curie-like  $1/T$  behavior is recovered. On the other hand, as expected for a system without broken symmetry, we have corroborated that the specific heat has also a rounded peak and then goes to zero as  $1/T^2$  for higher temperatures. Furthermore, the structure factor shows a sharp peak in the magnetic wave vector  $\mathbf{Q}_{\text{col}}$  that decreases with frustration and temperature. This means that despite the absence of long range order at finite temperature, AF Néel correlations are still dominant in our approximation.

The correct behavior obtained for the thermodynamic properties of the frustrated Heisenberg model lends support to the finite temperature approximation based on the modified spin wave theory. Regarding experiments, it should be noted that a quite different behavior is observed in the magnetic susceptibility on  $\kappa - \text{Cl}$ . At low temperatures, once long range AF order is developed, a weak ferromagnetism due to the canting of the AF order has been found [17]. Obviously, we do not expect to capture features inherent in the three dimensionality and the anisotropy of the compound with a 2D Heisenberg model. On the other hand, for higher temperatures the Curie's law is not found experimentally. Actually, for temperatures higher than 40K it is observed a crossover from a paramagnetic insulator to a metallic phase[18]. In order to take into account this crossover one should include the itinerancy of the electrons in the model, but for the present study of the AF phase it is not necessary. These differences do not allow a proper estimate of the value  $J'/J$  for the  $\kappa - \text{Cl}$  compound using our model, as it was performed recently for other related compounds[11]. Nevertheless, in the next section we show that the main features observed in NMR experiments can be qualitatively well reproduced by the frustrated model.

### III. $1/T_1$ NUCLEAR RELAXATION TIME

The  $1/T_1$  relaxation time is proportional to the transition probability of nuclear spin flips via their hyperfine interaction with the electronic spins. For an interacting localized spin model the relaxation mechanism is mediated by magnons. Single magnon processes are forbidden by energy conservation considerations but two magnon processes (Raman processes) –where one thermally excited magnon is destroyed and another is created in the nuclear spin flip process– are allowed[13]. Taking into account these processes, the relaxation time  $1/T_1$  can be related to the dynamic structure factor  $S(\mathbf{q}, \omega)$  as

$$\frac{1}{T_1} = \frac{1}{2N} \sum_{\mathbf{q}, \nu} A_\nu^2(\mathbf{q}) S(\mathbf{q}, \omega), \quad (4)$$

where  $A_\nu(\mathbf{q})$  is the hyperfine tensor and  $\omega$  is Larmor nuclear frequency. In what follows we assume  $A_\nu(\mathbf{q})$  isotropic and  $\mathbf{q}$  independent. As mentioned in section II within the linear spin wave theory  $S(\mathbf{q}, \omega) = S^{zz}(\mathbf{q}, \omega)$  and so the dynamic structure factor is defined as

$$S(\mathbf{q}, \omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt \langle \delta S_{\mathbf{q}}^z(t) \delta S_{-\mathbf{q}}^z(0) \rangle e^{i\omega t}.$$

Therefore, considering only longitudinal spin fluctuations

$$\delta S_{\mathbf{q}}^z = N^{\frac{1}{2}} \sum_{\mathbf{q}_1, \mathbf{q}_2} \delta_{\mathbf{q}_1 + \mathbf{q} + \mathbf{Q} - \mathbf{q}_2} [a_{\mathbf{q}_1}^\dagger a_{\mathbf{q}_2} - \langle a_{\mathbf{q}_1}^\dagger a_{\mathbf{q}_2} \rangle],$$

the two magnon structure factor results[19]:

$$S(\mathbf{q}, \omega) = \sum_{\mathbf{k}} (u_{\mathbf{k}} u_{\mathbf{k}+\mathbf{q}} + v_{\mathbf{k}} v_{\mathbf{k}+\mathbf{q}})^2 n_{\mathbf{k}} \times (1 + n_{\mathbf{k}+\mathbf{q}}) \delta(\omega_{\mathbf{k}} - \omega_{\mathbf{k}+\mathbf{q}} + \omega). \quad (5)$$

The relaxation time, Eq. (4), can be written as [20]

$$1/T_1 = \frac{1}{2} \int \rho^2(\epsilon) n_\epsilon (1 + n_\epsilon) \left(1 + \frac{\gamma_\epsilon^2}{\epsilon^2}\right) d\epsilon. \quad (6)$$

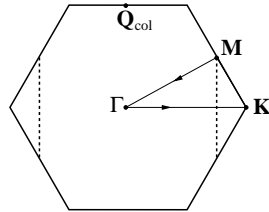


FIG. 4: Brillouin zone for the triangular lattice. The dashed lines,  $\mathbf{k} = (\pm\pi, k_y)$ , correspond to the dispersionless spin wave modes.

where  $\rho(\epsilon) = 1/N \sum_{\mathbf{k}} \delta(\epsilon - \omega_{\mathbf{k}})$  is the magnon density of states. For all  $T$  the spin wave spectrum has two dispersionless lines located at  $\mathbf{k} = (\pm\pi, k_y)$  (dashed lines in Fig. 4) deriving in a van Hove singularity in the density of states. These spin wave excitations correspond to antiferromagnetic fluctuations along the  $x$  direction. In Fig. 5 it can be seen that as temperature increases a gap opens at the Goldstone modes ( $\mathbf{k} = \mathbf{0}, \mathbf{Q}_{col}$ ), while the energy of the dispersionless lines goes downward to the gap value. If the system is frustrated, at a certain temperature, the dispersionless lines reach the bottom of the spectrum, and a larger number of excitations becomes nearly degenerate with them (see inset of Fig. 5). The availability of this large number of nearly degenerate magnon excitations produces a sharp increase of  $1/T_1$  (the integral in eq.(6) is dominated by the van Hove singularity of the magnon density of states). At higher temperatures the energy at  $\mathbf{k} = \mathbf{0}, \mathbf{Q}_{col}$  becomes greater than the energy at  $\mathbf{k} = (\pm\pi, k_y)$ , the large degeneracy disappears, and  $1/T_1$  goes down to a constant value inversely proportional to  $J'/J$ . It is worth noticing that without frustration the large degeneracy mentioned above never occurs, and  $1/T_1$  behaves monotonically.

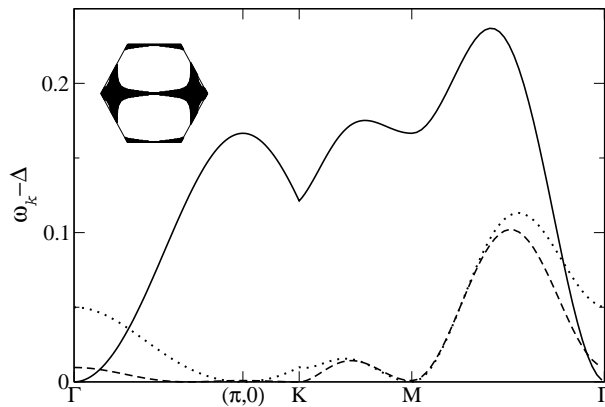


FIG. 5: Spin-wave dispersion, relative to the gap  $\Delta$ , along the  $\Gamma \rightarrow K \rightarrow M \rightarrow \Gamma$  line (shown in Fig.4), as a function of temperature for  $J'/J = 0.2$ . Solid curve:  $T = 3J$ . Dashed curve:  $T = 4.4J$ . Dotted curve:  $T = 5J$ .  $T = 4.4J$  is the temperature of the  $1/T_1$  peak. In the inset it is shown the region of nearly degenerate spin wave modes for  $T = 4.4J$  (see text).

### A. Effect of pressure

In this section we address the role of frustration in the insulating phase of the  $\kappa - Cl$ , and its possible relation with the effect of pressure. To this end, we compare the frustration dependence of the relaxation time predicted by the antiferromagnetic Heisenberg model with previous experimental results of the  $\kappa - Cl$  compound under pressure[3]. We have evaluated eq.(4) at  $\omega = 0$  since for realistic values  $\omega \ll J$ . In the next section the model predictions with varying  $\omega$  will be discussed. In Fig. 6 it is shown  $1/T_1$  as function of temperature for several values of frustration.

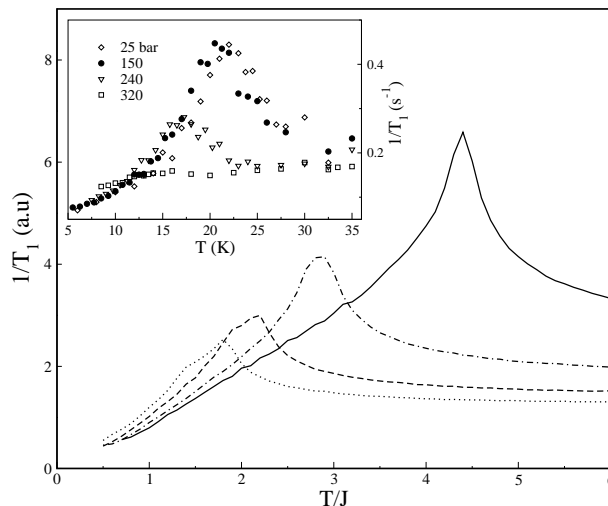


FIG. 6: Relaxation rate  $1/T_1$  versus temperature for several values of frustration:  $J'/J = 0.2$  (solid line),  $0.3$  (dot-dashed),  $0.4$  (dashed), and  $0.48$  (dotted). Inset: experimental data under pressure taken from ref.[3]

The effect of frustration is to suppress the  $1/T_1$  peaks and move them to lower temperatures. A similar behavior can be observed in previous NMR experiments [3] on  $\kappa - Cl$  compound under pressure (see inset Fig. 6). We also find that the  $1/T_1$  peak temperatures scale as  $J^2/J'$ . In terms of Hubbard parameters,  $J = 4t^2/U$ , if we assume that the effect of pressure is to decrease  $U/t$ , then  $J$  increases with pressure. Therefore, in order to reproduce the experimental behavior,  $J'/J$  should increase with pressure independently of the value of  $J$ . This analysis allows us to conjecture the existence of a close relation between the magnetic frustration and the macroscopic effect of pressure on the AF phase of  $\kappa - Cl$ . It is worth noticing that within our model it is required an appreciable variation of  $J'/J$  to mimic the experimental results. Similar conclusions has been recently pointed out by other authors in the context of Hubbard models[6, 7, 21]. Assuming the existence of this relation and the fact that, in our theory, the  $1/T_1$  peaks only appear with frustration, it can be said that at ambient pressure the  $\kappa - Cl$  compound is frustrated, and that its magnetic frustration does not change in a range of pressure up to  $\sim 150$  bar (see inset of Fig. 6).

From Figs. 3 and 6 it can be observed that the theoretical  $1/T_1$  peaks occur at higher temperatures than the uniform susceptibility ones. This is not what is expected, but we ascribe this feature to the modified spin wave approximation. In particular the constraint of zero magnetization is not rigorously implemented site by site. Instead, it has been imposed on average and this produces, at finite temperature, an underestimation of thermal fluctuations, which is manifested in the shift to higher temperatures of the  $1/T_1$  peaks. This aspect of the approximation has been also pointed out in another related frustrated model[22].

### B. Effect of magnetic field

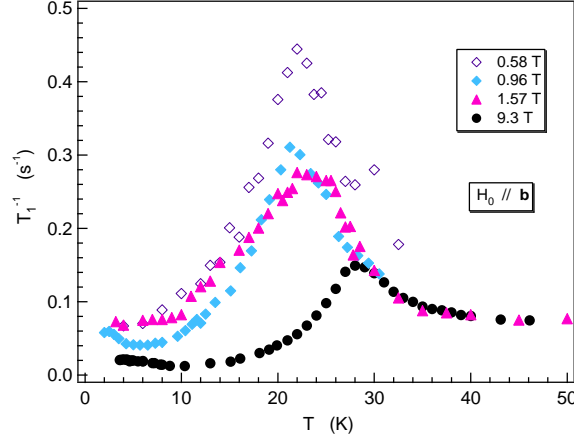


FIG. 7: Relaxation rate  $1/T_1$  vs. magnetic field at ambient pressure.

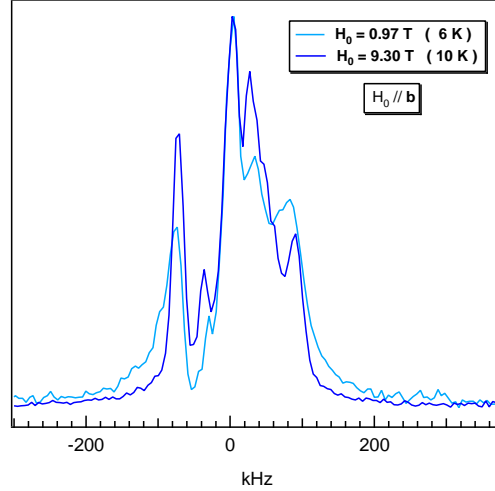


FIG. 8: NMR spectra of the  $\kappa - Cl$  compound at ambient pressure for two different values of the magnetic field.

In this section we show our measurements of the  $1/T_1$  nuclear relaxation time under magnetic field, and we compare them with the predictions of the frustrated spin model. All measurements were performed on single crystals with typical dimensions of  $0.8 \times 0.7 \times 0.07 \text{ mm}^3$ . The samples were cooled slowly ( $0.35 \text{ K/min}$ ) through the  $80 \text{ K}$  region in order to avoid the effects of imperfect ethylene ordering on the ground state[23]. Proton spin-lattice relaxation times have been measured using standard saturation-recovery technique where, depending on the linewidth conditions,

either free induction decay or spin-echo sequence were used to record the signal intensity.

A feature of geometrically frustrated materials is the shift towards low energy of the spectral weight of the magnetic excitations, which could be associated with a low spin dynamics with characteristic frequencies  $\omega \ll J$  [24]. This behavior results in a strong magnetic field dependence of  $1/T_1$ . Indeed, it is well known that a frequency dependent relaxation rate is expected in systems where fluctuation timescales are comparable with the inverse of the Larmor frequency [25]. In this section we present the  $1/T_1$  frequency dependence measurements. Figure 7 shows the evolution of the  $1/T_1$  peak for a broad range of magnetic fields. It is observed a strong suppression of the  $1/T_1$  peak with increasing magnetic field, along with an unexpected shift towards higher temperatures of the 3D Néel temperature. For most of the antiferromagnetically ordered compounds the Néel temperature is rather stable in the range of magnetic fields we have studied, and under stronger fields the Néel temperature tends to decrease. This standard evolution can be attributed to the fact that strong fields favour a more paramagnetic phase. Contrary, in our case we find an increase of the Néel temperature with magnetic field as well as a rather insensitive AF magnetization (as can be deduced from Fig. 8). This phenomenon, which is not clearly understood, has also been observed in a related  $\kappa$ -compound[26].

To investigate the model prediction we have considered the effect of the perpendicular magnetic field on the relaxation time by just varying the proton frequency  $\omega$ . Since the NMR spectra do not change noticeably with magnetic field, as it is shown in Fig. 8, we assume in the following that the field-dependent  $1/T_1$  is a *frequency effect*. For the same reason, we have neglected the canting of the magnetic order in the effective Hamiltonian. In Fig. 9 we show the relaxation time predicted by the frustrated model for different values of frequency and a generic value of  $J'/J$ . It can be seen that the frustrated model captures the strong suppression of  $1/T_1$  with increasing magnetic field observed experimentally (Fig. 7). The  $1/T_1$  behavior is similar for other moderate frustration values, while for the unfrustrated case it does not show a strong suppression with frequency. Note that the values of  $\omega$  are at least one order of magnitude lower than the magnetic frustration  $J'/J$  or the gap at the peak temperature. This strong frequency dependence of  $1/T_1$ , characteristic of systems with slow spin dynamics, is another indication that the  $\kappa$ -Cl compound at ambient pressure exhibits magnetic frustration.

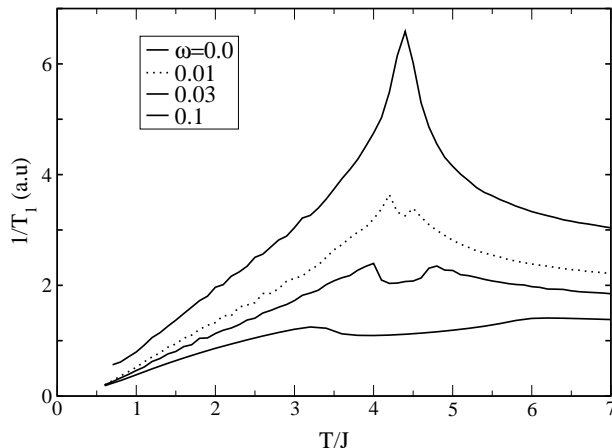


FIG. 9: Relaxation rate  $1/T_1$  versus temperature for several values of frequency and  $J'/J = 0.2$ .  $\omega$  is given in units of  $J$ .

In addition, the theoretical results show a double peak structure, which becomes more pronounced for larger frequencies. As a consequence of the energy conservation of the Raman processes with  $\omega \neq 0$  (i.e., the delta function in eq. (6))  $1/T_1$  gets dominated by the large density of states around the dispersionless lines  $\mathbf{k} = (\pm\pi, k_y)$  and around the  $\mathbf{k} = \mathbf{0}, \mathbf{Q}_{col}$  modes. As temperature varies, the peaks appear when the energy difference between both regions is  $\sim \pm\omega$ . It is worth to mention that although we capture the strong suppression of the  $1/T_1$  peak, we miss the shift of the 3D transition temperature and the magnetic field independence of  $1/T_1$  for high temperatures found experimentally (see Fig. 7). The latter might be due to the crossover from the paramagnetic insulator to the metallic phase above 40K.

#### IV. CONCLUDING REMARKS

We have measured the magnetic field dependence of the  $1/T_1$  relaxation time in the antiferromagnetic phase of the quasi-bidimensional organic compound  $\kappa - (BEDT - TTF)_2Cu[N(CN)_2]Cl$ . We have observed a strong field



dependence of  $1/T_1$ , characteristic of frustrated magnetic systems, due to a very slow spin dynamics[24]. We have also found an unexpected shift of the Néel temperature towards higher temperatures under magnetic field. A similar finding has been reported in the  $\kappa$  compound with  $X = Cu[N(CN)_2]Br$  [26]. To analyze our NMR measurements under magnetic field, along with previous ones performed under hydrostatic pressure[3] we have used the spatially anisotropic triangular Heisenberg model as a minimal model for the AF phase of the  $\kappa - Cl$ . We have treated the spin model with a linear spin wave calculation, modified to take into account the basic features of the 2D antiferromagnetic spin fluctuations at finite temperature. We calculated the  $1/T_1$  relaxation time considering Raman processes, simultaneous creation and destruction of magnons. We have studied the model predictions as a function of frustration and magnetic field. The latter has been considered as frequency effect, since the NMR spectra do not change noticeably in the range of the applied magnetic fields. Regarding the pressure dependence of the  $1/T_1$  relaxation time, we have found that the observed strong suppression and shift to lower temperatures of the  $1/T_1$  peaks under pressure can be qualitatively reproduced by an increase of the frustration in the Heisenberg model. Within the context of the microscopic model such shift corresponds to a genuine increase of the magnetic frustration  $J'/J$ , independently of the variation of  $J = 4t^2/U$  driven by pressure. These results are in line with recent works using Hubbard models, that emphasize the relevance of the role of frustration and its possible relation with pressure[6, 7, 21], besides the expected decrease of electronic correlation with pressure. On the other hand, Campos *et al.*[5], performing a Hückel tight binding study for a related  $\kappa$  compound, have found that the effect of hydrostatic pressure is to increase the frustration due to the sliding of the BEDT-TTF molecules in the dimers, one with respect to the other, along their short axes. This study also points out that the magnetic frustration is increased under pressure. However, the studies based on minimal microscopic models require large variation of  $U/W$  and frustration with pressure for a quantitative agreement with experiments[6], while the electronic calculations predict a slight variation of the tight binding parameters and, as a consequence, to a slight variation of the correlation and frustration.[1]. A possible explanation of this discrepancy is the fact that the electronic correlation dramatically renormalizes the bare tight binding parameters, as have been found recently by Liu *et al.*[21]. We would like to emphasize that we do not intend to give here a microscopic description of the pressure since we used an effective correlated model that do not include the actual structure of the  $\kappa - Cl$  compound. The task of describing on equal foot the real structure of the compound and the electronic correlation is a challenge outside the scope of the methods available at the present time.

Concerning the magnetic field dependence of the  $1/T_1$  peaks, the frustrated spin model also reproduces the strong suppression observed experimentally for Larmor frequencies  $\omega \ll J$ . This is another indication that the AF insulating phase of the  $\kappa - Cl$  compound is a frustrated antiferromagnet even at ambient pressure. However we can not reproduce the shift to higher temperatures of the  $1/T_1$  peak under magnetic fields, an issue that deserves further investigation.

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- [1] R. H. McKenzie 1997, Science **278**, 820; R. H. McKenzie 1998, Comments Cond. Mat. **18**, 309.
  - [2] N. P. Ong and R. J. Cava 2004, Science **305**, 52.
  - [3] S. Lefebvre, P. Wzietek, S. Brown, C. Bourbonnais, D. Jérôme, C. Mézière, M. Fourmigué, and P. Batail 2000, Phys. Rev. Lett. **85**, 5420.
  - [4] P. Limelette, P. Wzietek, S. Florens, A. Georges, T. A. Costi, C. Pasquier, D. Jerome, C. Mézière, and P. Batail 2003, Phys. Rev. Lett. **91**, 16401.
  - [5] C. E. Campos, P. S. Sandhu, J. S. Brooks, and T. Ziman 1996, Phys. Rev. B **53**, 12725.
  - [6] B. J. Powell and Ross H. McKenzie 2005, Phys. Rev. Lett. **94**, 047004.
  - [7] J. Y. Gan, Yan Chen, Z. B. Su, and F. C. Zhang 2005, Phys. Rev. Lett. **94**, 067005.
  - [8] A.E. Trumper 1999, Phys. Rev. B, **60**, 2987; J. Merino, R. H. McKenzie, J. B. Marston, and C. H. Chung 1999, J. Phys.: Condens. Matter **11**, 2965.
  - [9] L. O. Manuel and H. A. Ceccatto 1999, Phys. Rev. B **60**, 9489.
  - [10] Z. Weihong, R. H. McKenzie, and R. P. Singh 1999, Phys. Rev. B **59**, 14367.
  - [11] W. Zheng, R. R. P. Singh, R. H. McKenzie, and R. Coldea 2005, Phys. Rev. B **71**, 134422.
  - [12] M. Takahashi 1987, Phys. Rev. Lett. **58**, 168.
  - [13] D. Beeman and P. Pincus 1968, Phys. Rev. **166**, 359. N. Bulut, D. W. Hone, D. J. Scalapino, and N. E. Bickers 1990, Phys. Rev. B **41**, 1797. F. Mila, D. Poilblanc, and C. Bruder 1991, Phys. Rev. B **43**, 7891. S. Yamamoto 2000, Phys. Rev B **61** R842.
  - [14] K. Miyagawa, A. Kawamoto and K. Kanoda 2002, Phys. Rev. Lett. **89**, 017003.
  - [15] N.D Mermin and H. Wagner 1966, Phys. Rev. Lett. **17**, 1133.
  - [16] A. Auerbach and D. P. Arovas 1988, Phys. Rev. Lett. **61**, 617.
  - [17] Y. Shimizu, K. Miyagawa, K. Kanoda, M. Maesato, and G. Saito, 2003 Phys. Rev. Lett., **91**, 017001.
  - [18] F. Kagawa, T. Itou, K. Miyagawa, and K. Kanoda 2004, Phys. Rev. Lett. **93**, 127001.

- [19] I. U. Heilmann, J. K. Kjems, Y. Endoh, G. F. Reiter, G. Shirane, and R. J. Birgeneau 1981, Phys. Rev. B **24**, 3939.
- [20] F. Mila and T. M. Rice 1989, Phys. Rev. B **40**, 11382.
- [21] J. Liu, J. Schmalian, and N. Trivedi 2005, Phys. Rev. Lett. **94**, 127003.
- [22] N. B. Ivanov and P. Ch. Ivanov 1992, Phys. Rev. B **46**, 8206.
- [23] A. Kawamoto, K. Miyagawa, and K. Kanoda 1997, Phys. Rev. **55**, 14140.
- [24] A. P. Ramirez 2001, *Handbook of Magnetic Materials*, edited by K. H. J. Buschow (Elsevier, New York), Vol. 13.
- [25] see, for example: *Multidimensional Solid-State NMR And Polymers*, K.Schmidt-Rohr and H.W.Spiess, Academic Press 1994.
- [26] P. Wzietek, H. Mayaffre, D. Jerome, and S. Brazovskii 1996, J. Phys. I France **6**, 2011.